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Unsymmetrical Three-Dimensional Macromolecules: Preparation and Characterization of Strongly Dipolar Dendritic Macromolecules

Karen L. Wooley,[†] Craig J. Hawker,[‡] and Jean M. J. Fréchet*

Contribution from the Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301

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Abstract: The preparation and characterization of a series of strongly dipolar monodisperse dendritic molecules ranging in molecular weight from 604 to 10 530 are described. The molecules are designed to achieve high dipole moments through the placement of electron-withdrawing cyano groups and electron-donating benzyloxy groups at segmentally opposed regions of the chain ends of the dendrimers. This is accomplished through application of the convergent growth approach in the preparation of dendritic benzyl ether fragments bearing the appropriate chain ends, followed by stepwise attachment to a linear difunctional core molecule, 4,4′-dihydroxybiphenyl. For comparison purposes, a series of symmetrical unfunctionalized dendritic benzyl ethers with molecular weights from 791 to 13 526 were also prepared. Dipole moment values were calculated from measurements of capacitance and refractive index. The dipole moments of the functionalized dendrimers were much larger than those for the symmetrical structures and increased with increasing molecular weight. In contrast to the behavior of linear polymers, plots of dipole moment *vs* molecular weight for the dendritic molecules were not linear. This is attributed to steric effects that affect the shape of the dendritic structures with the adoption of an increasingly globular shape as the molecular size increases. This shape change affects the net contribution of a large number of polar functionalities to the overall vector addition of the dipole moment.

Introduction

As the perceived need for smaller and more efficient components in mechanical, electronic, and optical devices increases, more research is being devoted to nanotechnological development including the preparation of molecular machines,[1] electrooptic switches,[2] and new types of nonlinear optical systems.[3] In order to reach these objectives, novel macromolecular architectures and materials exhibiting unusual physical properties are required. Dendritic macromolecules, having well-defined structures and a high degree of control over the local composition, offer a unique opportunity for extension of unusual architecture toward the production of molecular devices.

Dendritic macromolecules[4] are globular three-dimensional structures containing at least one branch juncture at each monomer unit and a large number of chain ends, which result in solubility, viscosity, reactivity, and thermal behaviors differing from those of linear polymers. These structures may be regarded as extremely small particles with diameters of ca. 30–100 Å, and the ability to control the number and placement of chain end functionalities[5] allows much versatility in the modification or tuning of their properties.

Because of the compact, globular shape of dendritic macromolecules, their orientation in alignment with an external electric field may be analogous to or even less restricted than that for rigid linear systems such as rod-like liquid crystals. As a first approach in the design of globular molecules that can be oriented in an external field, we have prepared unsymmetrically functionalized dendritic molecules designed to possess large dipole moments. The target molecules have electron-donating and electron-withdrawing groups placed in two segregated and opposed segments at the chain ends (periphery) of the dendritic molecules. As a consequence of their unsymmetrical functionalization, these molecules in the aligned state are also expected to have hemispheres with differing optical properties.

Results and Discussion

Synthesis. The preparation of dipolar dendritic molecules is begun with the synthesis of dendritic fragments containing electron-withdrawing groups and fragments containing electron-donating groups at the chain ends. Cyano groups were chosen as the electron-withdrawing groups because of their strong electron withdrawal and their stability[5b] to the reaction conditions used for dendritic growth with 3,5-dihydroxybenzyl alcohol as the monomer unit. Benzyloxy groups were chosen as the electron-donating substituents to simplify the synthesis, as fragments containing these chain ends have been prepared before.[6] Stepwise

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[†] Current address: Washington University, Department of Chemistry, St. Louis, MO 63130-4899.

[‡] Current address: IBM Almaden Research Center, San Jose, CA 95120.

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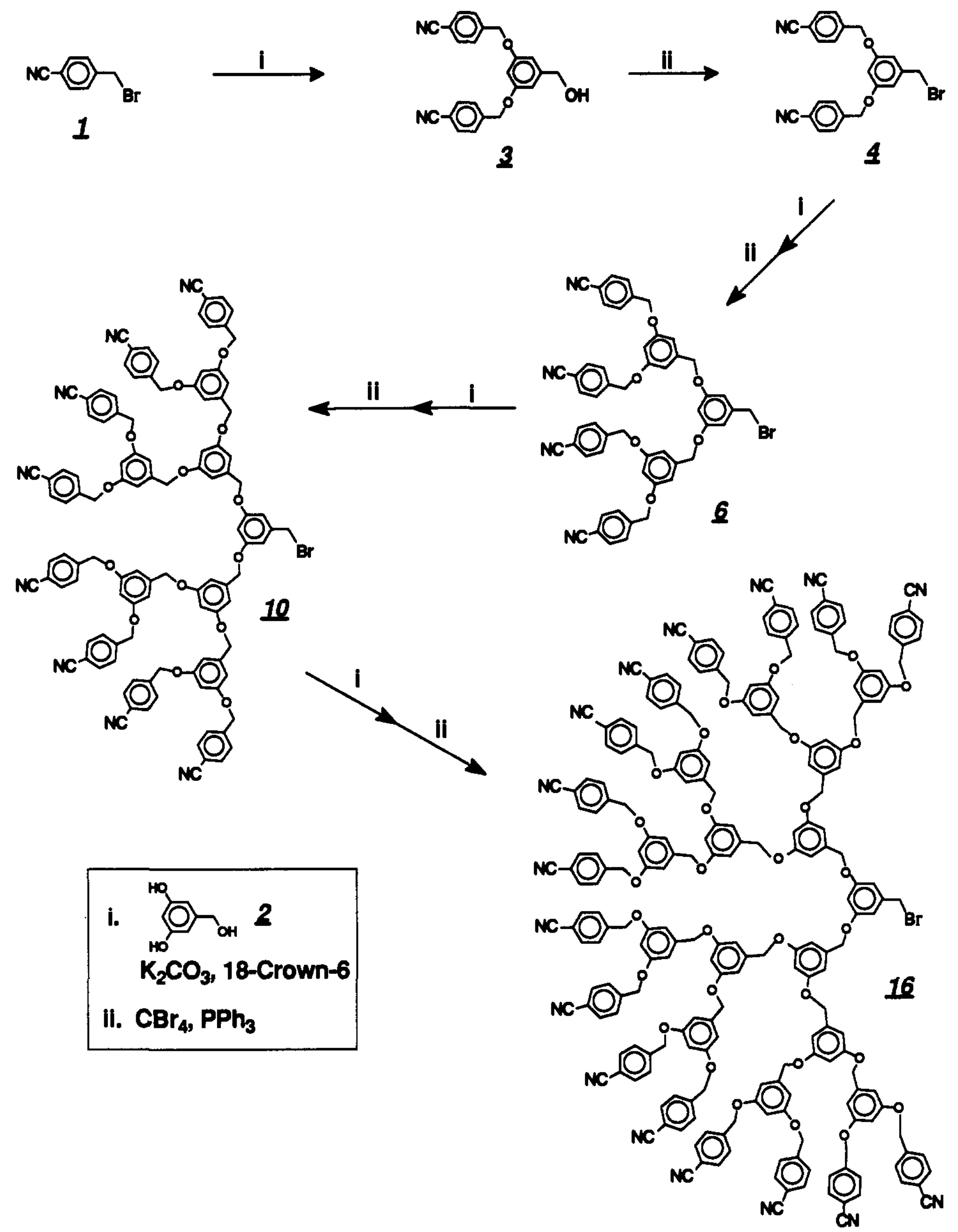
Scheme I

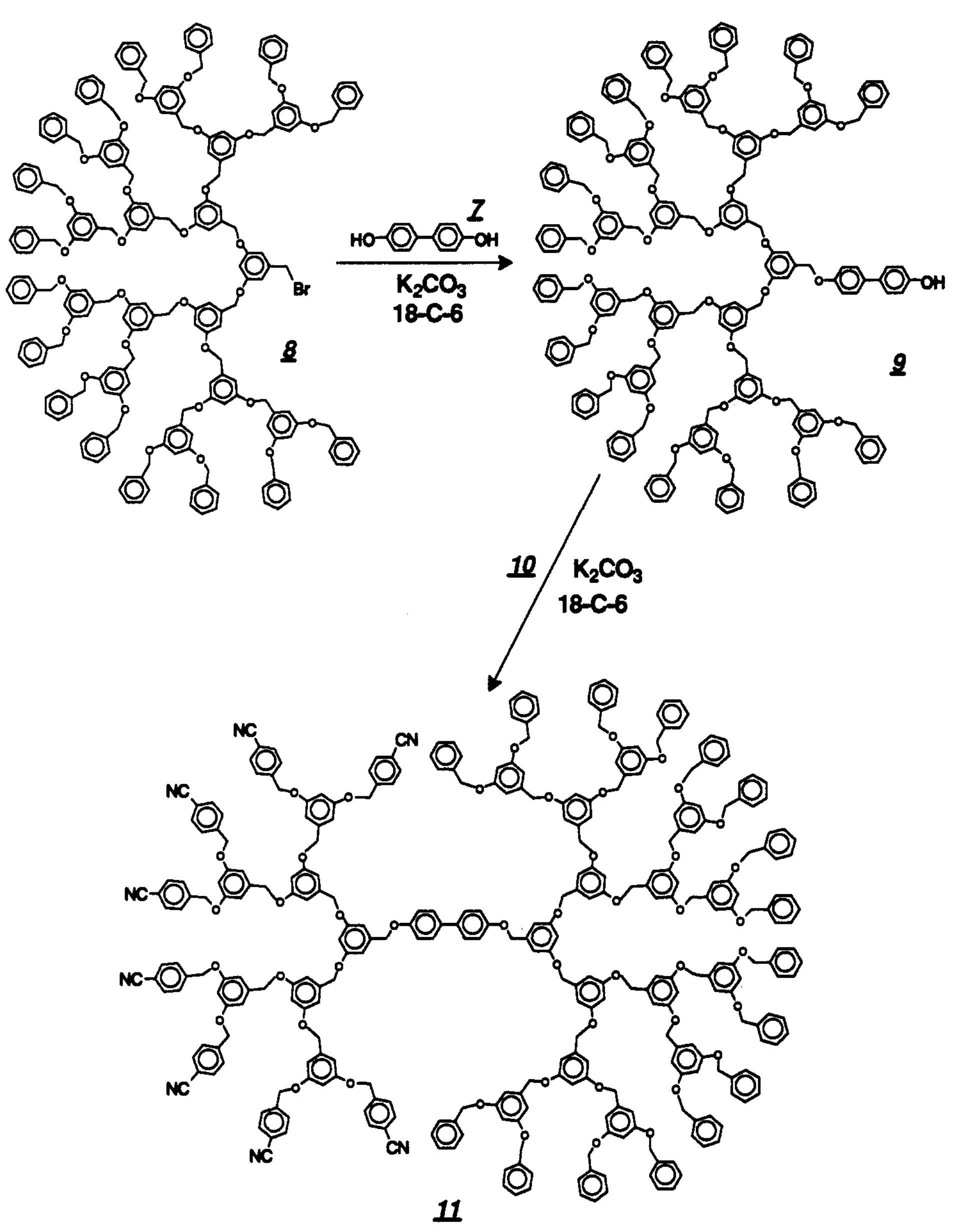


attachment of the preformed dendritic fragments to a difunctional core molecule will then afford the final dipolar dendritic products.

Scheme I shows the preparation of cyano-terminated dendritic fragments by the convergent growth approach[6] involving repetitive sequential growth and activation steps. The synthesis is begun with 4-(bromomethyl)benzonitrile, **1**, which is coupled to the monomer unit, 3,5-dihydroxybenzyl alcohol, **2** in the presence of potassium carbonate, in acetone heated at reflux to give the first-generation alcohol, $(CN)_2$-[G-1]-OH, **3**, in 91% yield. It is interesting to note that no products from C-alkylation are observed, while the tri-O-alkylated product is isolated in ca. 7% yield. This is in contrast to the previous reactions we have studied involving other benzylic bromides[5,6] and may be due to the strong electron-withdrawing effect of the cyano group that increases reactivity of the benzylic halide moiety. Reaction of $(CN)_2$-[G-1]-OH, **3**, with carbon tetrabromide/triphenylphosphine regenerates the benzyl bromide site at the focal point to give $(CN)_2$-[G-1]-Br, **4**. Coupling of **4** to the monomer unit, **2**, through reaction with potassium carbonate affords the second-generation dendritic alcohol, $(CN)_4$-[G-2]-OH, **5**. In this reaction, and all further coupling reactions to the monomer unit, no tri-O-alkylated or C-alkylated products were observed, in agreement with previous findings.[5,6] Activation of the benzylic alcohol at the focal point[6] of the dendrimer to the reactive benzylic bromide was again by reaction of **5** with carbon tetrabromide and triphenylphosphine to yield $(CN)_4$-[G-2]-Br, **6**. Repetition of this two step process leads to higher generations, with the number of cyano terminal units increasing by a factor of 2 with each increase in generation number. A well-known characteristic of the convergent growth approach is that a single reactive group located at the focal point is used for generation growth (i.e., the benzyl alcohol or bromide group of **3**, **4**, **5**, **6**, **10**, **16**, etc.).

Our target structures consisted of a linear bifunctional core moiety substituted on one end with a cyano-substituted dendrimer of generation n, and in an effort to negate the effects of the internal building blocks despite the lack of conjugation, the opposite end was coupled to an unsubstituted dendrimer of generation $n + 1$. This is accomplished through stepwise alkylation of the difunctional core molecule, 4,4'-dihydroxybiphenyl, **7**. As shown in Scheme II, reaction of the unsubstituted dendritic fragment, [G-4]-Br,[6] **8**, with a large excess of 4,4'-dihydroxybiphenyl, **7**, gives the monoalkylated product, **9**, containing a single phenolic group at the focal point, in 64% yield. Reaction of **9** with CN_8-[G-3]-Br, **10**, gives a 73% yield

Scheme II



of the dipolar dendritic molecule **11** containing eight electron-withdrawing cyano groups on one half of the structure and 16 electron-donating benzyloxy groups on the opposite half. Since the net electronic vector corresponding to the 3,5-dibenzyloxy-substituted aromatic rings can be considered equivalent to the vector of a benzyloxy substituent in the 4-position, the electronic vector of the eight electron-withdrawing cyano groups is effectively opposed by the vector addition of eight electron-donating benzyloxy groups, Similar dipolar dendritic molecules of molecular weights from 604 to 10 530 (Figure 1) were prepared by this process using dendritic fragments of different generation numbers. Because R_f differences between the unfunctionalized monophenolic derivatives and the dipolar products containing cyano groups are large, while the R_f differences between the cyano-terminated dendritic fragments and the products are small, a slight excess of the monophenolic species is used in this final coupling reaction to aid in chromatographic purification. Due to the large molecular weight increase (ca. 50% increase) upon attachment of the cyano-substituted dendritic unit, size exclusion chromatography was useful in monitoring these reactions and also in verifying the purity of the products.

For comparison of dipolar properties and magnitudes of dipole moments, symmetrical dendritic molecules were prepared by attachment of two benzyl ether-terminated dendritic fragments to the bisphenolic core molecule, 4,4′-dihydroxybiphenyl, **7**, As shown in Scheme III, reaction of 2.1 equiv of [G-4]-Br, **8**, with 4,4′-dihydroxybiphenyl, **7**, and potassium carbonate in acetone heated at reflux gives [G-4]-[C]-[G-4], **12**, in 84% yield after purification. Again, a series of these dendritic molecules of increasing sizes were prepared with molecular weights ranging from 791 to 13 526.

Throughout this paper, structures are drawn two-dimensionally as planar, flat molecules, However, steric and entropic considerations dictate that the molecules adopt a three-dimensional globular structure. The transition from an extended to a globular conformation has been observed near the fourth generation for dendrimers consisting of benzyl ether units by light scattering,[6] viscosity,[7] and solvatochromic measurements[8] and by photoinduced electron transfer measurements for starburst amidoamines.[9] As will be described in the following text, dipole moment

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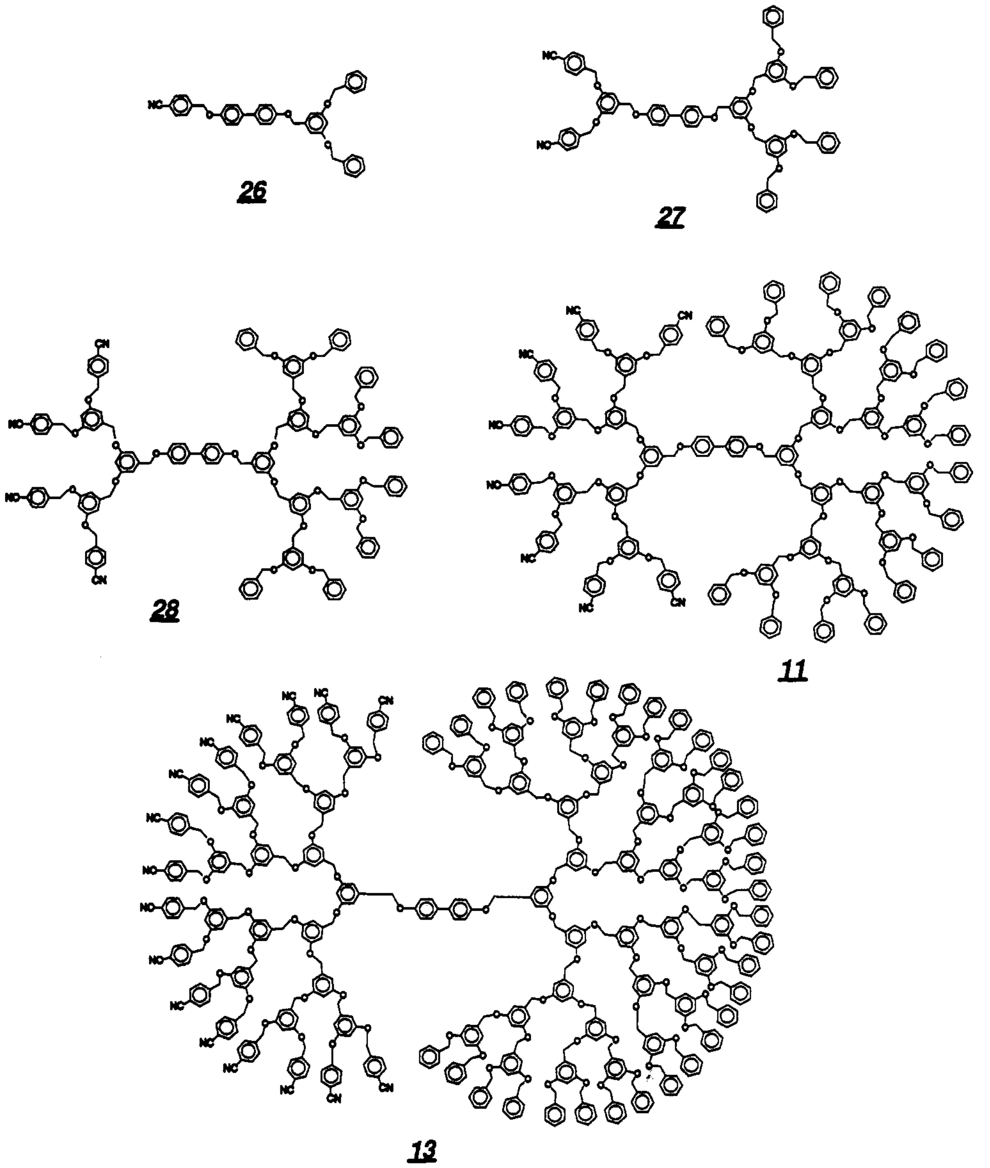
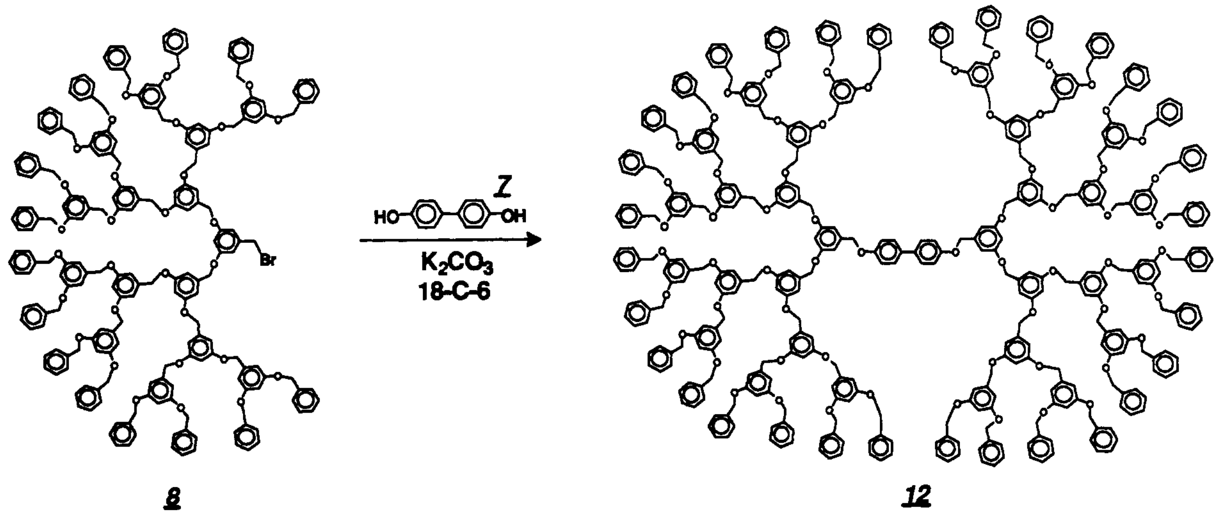


Figure 1. Dipolar dendritic macromolecules **26**, **27**, **28**, **11**, and **13**, with molecular weights ranging from 604 to 10 530 and μ values from 4.5 to 17.6 D.

Scheme III



measurements and refractive index studies also seem to confirm the globular nature of the dendritic macromolecules. It should be mentioned that the shape change, periodic properties of dendrimers, as a function of generation, were first predicted by Goddard et al.[4b] for PAMAM Starburst dendrimers as early as 1989.

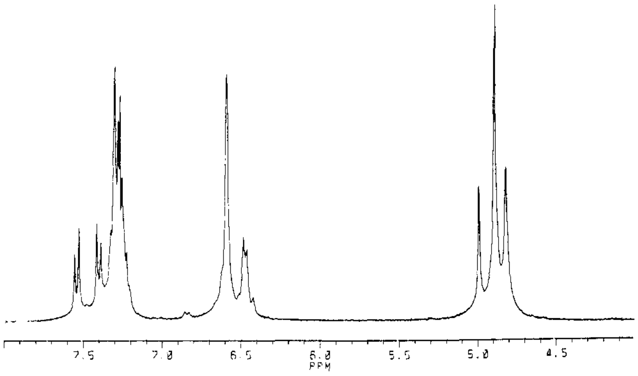


Figure 2. ^1H NMR spectrum (300 MHz, $CDCl_3$) of dipolar dendritic macromolecule **13**.

Characterization. Each of the compounds prepared was fully characterized by standard techniques. Figure 2 shows the ^1H NMR spectrum for the largest dendritic dipolar macromolecule prepared, CN_{16}-[G-4]-[C]-[G-5], **13**, in which a great deal of structural information is present. The quartet (ABq) at 7.56 and 7.42 ppm and the singlet at 5.01 ppm correspond to the aromatic and the benzylic methylene protons, respectively, of the cyano-substituted chain ends. The resonance at 6.86 ppm is one-half of the ABq for four of the core protons. Integration of these resonances and comparison with other resonances in the spectrum allow the number of cyano and unsubstituted chain ends as well as the sizes of the dendritic units to be determined. Confirmation of structure for all other products was similarly accomplished, in fact with higher precision, due to their smaller sizes. In the ^1H NMR spectra, the resonances for the protons of the core were indicative of the substituents attached to the core. For the symmetrical, dialkylated molecules, only a single ABq is observed, while the monoalkylated core protons resonate as two observable ABq's. The dipolar molecules exhibit two ABq's at lower generations (smaller sizes), where the core is near the unequivalent chain end functionalities, which merge into one ABq at higher generations. This may be due to a combination of peak broadening and the increasing homogeneous and symmetrical nature of the internal composition of the structure as the chain ends become farther removed from the core unit. Similar structural information was obtained from the ^{13}C NMR spectra. For example, the core molecule showed either four or eight distinct resonances, depending on the symmetry of the substitution. Each of the resonances was accurately assigned using standard theoretical values and equations,[10] and the layers of monomer units for the different generations were seen as additional peaks slightly shifted from one another.

Gel permeation chromatography (GPC) confirmed that each of the products was a single monodisperse material. As has been previously reported[6] for dendritic benzyl ether macromolecules, the polystyrene equivalent molecular weights were smaller than the actual molecular weights, and this difference increased with increasing molecular weights of the compounds. In addition to GPC, reversed-phase liquid chromatography (10% THF/acetonitrile) was used in the determination of purity, from which the products were found to be greater than 99.5% pure.

Differential scanning calorimetry experiments demonstrated that the dipolar molecules containing blocks of differing chain end substitution behave as block copolymers with their glass transition temperatures being intermediate between those of the two parent blocks. However, as has been reported,[11] the observed T_g values do not fit the theoretical values calculated from equations[12] developed specifically for the estimation of T_g of *linear* block copolymers. For example, the T_g of CN_8-[G-3]-OH is 334 K, and the T_g of [G-4]-[C]-OH is 312 K. From these values, the T_g for the block copolymer CN_8-[G-3]-[C]-[G-4], **11**, is calculated as 320 K and experimentally is found to be 327 K. Although the theoretical and observed T_g values do not agree, the differences between their values decrease with increasing size of the dendritic macromolecules, as they approach $(T_g)_\infty$.

Dipole Moment Measurements. In addition to standard characterization techniques, the capacitance and refractive index increments were measured for benzene solutions of both families of unsymmetrical cyano-substituted and symmetrical unsubstituted dendritic molecules, thus allowing the calculation of dipole moments.[13,14] The dielectric constants, ϵ, were calculated from measurements of the capacitance of benzene solutions of the samples, according to the following equation:

$$\epsilon = \Delta C/\Delta C_{\text{air}} = (C - k)/(C_{\text{air}} - k) \qquad (1)$$

where C is the capacitance and k is a constant related to lead capacitance which was determined from measurements on samples of known ϵ. A plot of ϵ *vs* χ_2 (mole fraction of solute in solution) gives a straight line in which the y-intercept is indicative of the dielectric constant of the solvent. The slope of this line, a, was used in the calculation of the molar orientation polarization of the solute at infinite dilution, $P_{2\mu}{}^\circ$. The value of $P_{2\mu}{}^\circ$ was obtained from the Guggenheim–Smith equation:[15]

$$P_{2\mu}{}^\circ = \frac{3M_1}{\rho_1}\left(\frac{a}{(\epsilon_1 + 2)^2} - \frac{c}{(n_1{}^2 + 2)^2}\right) \qquad (2)$$

where M_1 is the molar mass of the solvent (benzene, 78.11 g/mol), ρ_1 is the density of the solvent (benzene, 0.874 g/mL), a is the slope of ϵ *vs* χ_2, ϵ_1 is the dielectric constant of the solvent (benzene, 2.284 at 293 K), n_1 is the index of refraction of the solvent (benzene, 1.5011 at 293 K), and c is the slope of a plot of the solution index of refraction, n *vs* χ_2. Alternatively, the same value for $P_{2\mu}{}^\circ$ was obtained by using the molecular weight of the macromolecule in place of M_1 along with the weight fraction of solute in place of the mole fraction χ_2 in the determination of a and c.

The dipole moments, μ, expressed in debyes (D) for the various compounds, were then calculated according to the following equation:

$$\mu = 0.0128(P_{2\mu}{}^\circ T)^{1/2}\ \text{D} \qquad (3)$$

Data collected from the measurements and calculations of dipole moment are given in Table I. The dipolar cyano-substituted dendritic molecules were indeed found to possess quite large values for dipole moments, with the dipole moment increasing with increasing molecular weight. Initially, the dipole moments measured for the unsubstituted, "symmetrical" molecules may appear surprisingly large. However, as emphasized earlier, the molecules do not exist as drawn in structures such as **12** and much flexibility exists, especially at lower sizes since dense-packing is not achieved. Rotation about any of the many bonds in the structure destroys the symmetry of **12** and contributes to the existence of dipolar arrangements. Application of an electric field results in significant distortion of the molecules from a symmetrical equilibrium conformation and, thus, enhances the observed dipole moment. This enhancement is expected to be greater for the smaller, more flexible structures and to decrease

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[15] See ref 14a, in which it has been shown that calculations based on the Debye and Halverstadt–Kumler equations give results in general agreement with those based on the Guggenheim–Smith equations.

Table I. Data for the Dipolar and Unsubstituted Dendritic Macromolecules

compound	no.	mol wt	*a*	*c*	$P_{2\mu}°$	μ	d*n*/d*c*
CN-[G-0]-[C]-[G-1]	**26**	604	36.0	1.01	511	4.54	0.1469 ± 0.0053
CN_2-[G-1]-[C]-[G-2]	**27**	1266	40.7	1.95	565	5.25	0.1393 ± 0.0051
CN_4-[G-2]-[C]-[G-3]	**28**	2589	118	4.42	1660	9.00	0.1483 ± 0.0008
CN_8-[G-3]-[C]-[G-4]	**11**	5236	242	8.42	3410	12.9	0.1447 ± 0.0009
CN_{16}-[G-4]-[C]-[G-5]	**13**	10 530	447	13.2	6330	17.6	0.1430 ± 0.0062
[G-1]-[C]-[G-1]	**22**	791	11.5	1.58	145	2.66	0.1770 ± 0.0101
[G-2]-[C]-[G-2]	**23**	1640	21.0	2.72	267	3.61	0.1496 ± 0.0016
[G-3]-[C]-[G-3]	**24**	3338	58.1	5.12	772	6.14	0.1385 ± 0.0027
[G-4]-[C]-[G-4]	**12**	6734	95.1	8.32	1270	7.87	0.1043 ± 0.0079
[G-5]-[C]-[G-5]	**25**	13 526	223	17.3	3000	12.1	0.1140 ± 0.0042

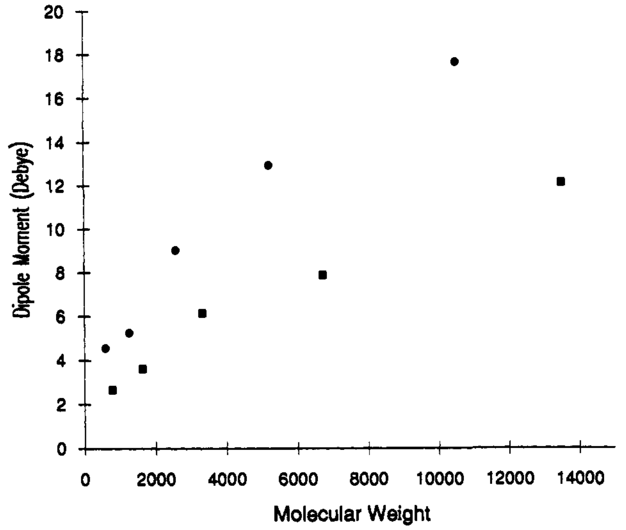

Figure 3. Overlay of plots of dipole moment *vs* molecular weight for dipolar dendritic molecules **26**, **27**, **28**, **11**, and **13** (●) and unfunctionalized dendritic molecules **22**, **23**, **24**, **12**, and **25** (■).

as steric crowding takes effect, restricting somewhat the orientation of individual dipole vectors. Supporting the high polarity findings are the results of experiments with solvatochromic probes placed at the focal point of benzyl ether dendrimers.[8] These experiments indicated that the interior of the dendrimer has a polarity similar to that of *N*,*N*-dimethylformamide. Contributions from distortion polarization of these structures may be quite large, but could not be subtracted.

Typically, the dipole moment of linear polymers[14,16–19] increases in a linear fashion with increasing degree of polymerization, and the dipole moment is often reported as the dipole moment ratio, D_r or $\varphi = \mu^2/N(\mu_0)^2$, where μ is the dipole moment of the polymer, N is the degree of polymerization, and μ_0 is the dipole moment of the monomer unit. However, attempts to fit the data obtained for dendritic molecules to this equation led to large deviations in the values of φ. This is likely due to the compact globular shape and the relatively low molecular weights of the dendritic structures that eliminate some of the average conformations available to linear random coil structures (for short linear chains, φ is not independent of N). Examination of the plots of μ vs molecular weight (Figure 3) demonstrates the nonlinearity of this relationship, which is in contrast to the behavior exhibited by linear polymers. This may be explained by a transformation in the dendritic structure from an extended and flexible conformation to a more rigid and less easily distorted conformation as a result of the applied electric field. As stated above, for small, flexible dendrimers, application of an electric field may cause alignment of the polar units of the structure in the direction of the field; thus, each of the polar units contributes to the overall dipole moment of the molecule. As the molecular weights of the dendritic molecules increase, they are forced to adopt a more globular structure. Simple geometric considerations indicate that as the globular shape is adopted, some of the monomer units as well as chain ends will be placed in locations where they are not able to fully align along the direction of the applied field and, therefore, their vector contributions to the overall dipole moment are attenuated. Since the dipole moment of a molecule is the combined vector addition of its constituents, this results in a reduction of the dipole moment of the dendritic molecules, in comparison to linear or less sterically confined systems. Therefore, the observed deviation from linearity in the plot of μ *vs* molecular weight can be taken as additional supporting evidence for the extended to globular shape change in dendritic macromolecules of higher generations. It is plausible that at even higher generations a maximum in μ would be observed; however, such large functionalized molecules are not readily accessible.

Refractive Index Increment. Due to the nature of growth of dendritic molecules, in which the mass increases exponentially while the volume increases cubically (after adoption of a globular shape), a maximum is observed in the plot of log intrinsic viscosity *vs* molecular weight. The reciprocal of intrinsic viscosity, corresponding to the solution density, would therefore be expected to exhibit a minimum. This leads also to the prediction of a minimum in the refractive index and in the refractive index increment, d*n*/d*c*, for dendritic molecules as the generation number increases. A minimum in the refractive index increment for dendritic benzyl ethers has been suggested,[7] but not experimentally confirmed. Precise measurements of the refractive index increment have been made for both the unsymmetrical cyano-substituted and symmetrical unsubstituted dendritic benzyl ether molecules (Table 1 and Figure 4). For the cyano-substituted dendrimers, a minimum in d*n*/d*c* is not observed and the value of d*n*/d*c* remains nearly constant. However, a minimum is observed in the value of d*n*/d*c* for the unsubstituted series of dendritic benzyl ethers. This minimum coincides with the maximum observed in intrinsic viscosity[7] and the discontinuity in solvatochromic behavior[8] with respect to molecular weight, for dendritic structures of the same composition. The minimum in both density and refractive index reported for dendritic polyamidoamines[4a] occurs at approximately the same generation number as our findings.

Conclusion

We have demonstrated the preparation of monodisperse dendritic macromolecules possessing enhanced dipole moments due to the presence of electron-donating and electron-withdrawing groups at opposed chain ends. Conceptually, these structures might be useful in the design of switching devices based on dipolar globular macromolecules. The ability to control the overall location of functionalities within dendritic globules may be further exploited for the creation of many other types of nanotechnological devices. For example, construction of one or more "layers" of the

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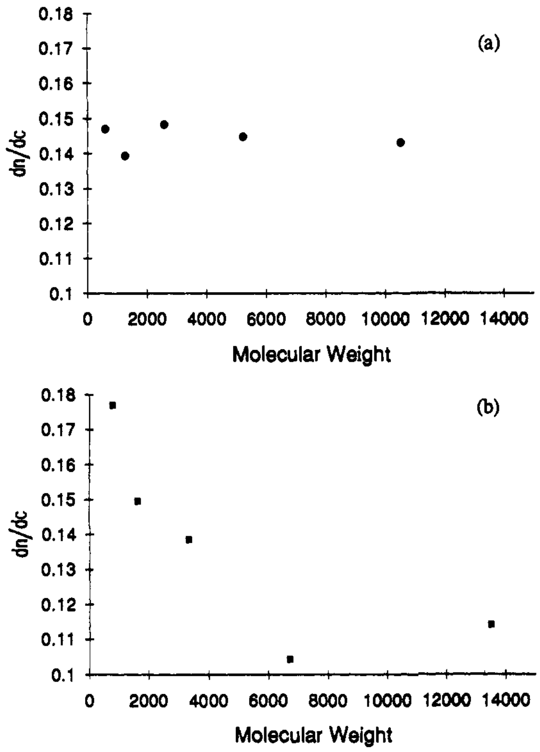

Figure 4. Plots of d*n*/d*c* *vs* molecular weight for (a) dipolar dendritic molecules **26**, **27**, **28**, **11**, and **13** (●) and (b) unfunctionalized dendritic molecules **22**, **23**, **24**, **12**, and **25** (■).

dendritic macromolecule from chromophoric monomer units, in conjunction with the electronically different chain ends as described herein, may result in enhancement of nonlinear optical properties while retaining the intrinsic switching ability of the globular dipole.

Experimental Section

Dipole Measurements. Dipole moments were calculated from independent measurements of capacitance and refractive index increment, which were experimentally determined as follows:

(a) Capacitance measurements were carried out at 22 °C for each sample with multiple readings on four solutions of varying concentrations in benzene (freshly distilled from potassium) from 0.05 to 2 wt % for the dipolar compounds and from 0.5 to 10 wt % for the unsubstituted compounds. The instrumentation consisted of a Wavetek 4-MHz function generator Model 182A; Tektronix 2213 60-MHz oscilloscope; Data Precision 2480 voltmeter; circuit board; precision air capacitor; and a 2-mL glass cell. Measurements at frequencies of 1 and 10 kHz gave the same value for dielectric constant, confirming that conductivity was not an influence in the capacitance measurements.

(b) Refractive index increments were measured from the same solutions as above, using a Wyatt Optilab 903 refractometer with gravity flow, and calculations were performed with Wyatt d*n*/d*c* software.

General Directions. Melting points and glass transition temperatures were measured by differential scanning calorimetry using a Mettler DSC 30 low-temperature cell coupled to a TC10A TA processor. Heating rates were 10 K/min. T_g was taken as the midpoint of the inflection tangent. Infrared spectra were recorded on a Nicolet IR/44 spectrophotometer as thin films on NaCl disks. ^{1}H NMR spectra were recorded on solutions in $CDCl_3$ on a Bruker AF300 (300 MHz) spectrometer with the solvent proton signal as standard. ^{13}C NMR spectra were recorded at 75 MHz on a Bruker AF300 spectrometer with $CDCl_3$ as the solvent and the solvent carbon signal as internal standard. Analytical TLC was performed on commercial Merck plates coated with silica gel GF_{254} (0.25 mm thick). Silica for flash chromatography was Merck Kieselgel 60 (230–400 mesh). Chromatotron plates were coated as 1-, 2-, or 4-mm thickness with silica gel 60 GF_{254}, particle size 5–40 μm (EM Science 7730). Size exclusion chromatography was carried out on an IBM LC/9560 chromatograph connected to a Milton Roy refractoMonitor IV refractive index detector; data analysis was performed with GPC-PRO software, version 3.12 (Viscotek Corp.). Three 5-μm Polymer Laboratories columns (300 × 7.7 mm) connected in series in order of increasing pore size (500 Å, 1000 Å, mixed bed C) were used with THF as solvent. Ar, Ar′, Ar″, and Ar‴ refer to the 1,3,5-substituted aromatic rings of the various monomer unit layers belonging to the dendrimers, where the generation number corresponds to the number of layers of monomer units.

General Procedure for the Synthesis of Dendritic Benzyl Alcohols. These reactions were carried out on scales varying from 5 to 10 g depending on generation number. For example, dendrimer **15** with 16 cyano chain ends was prepared on a scale of 6 g. A mixture of the appropriate dendritic benzyl bromide (2.05 equiv), 3,5-dihydroxybenzyl alcohol (**2**) (1.00 equiv), K_2CO_3 (2.2 equiv), and 18-crown-6 (0.2 equiv) in THF was heated at reflux and stirred vigorously under nitrogen for 24 h. The mixture was allowed to cool and evaporated to dryness under reduced pressure. The residue was partitioned between water and $CHCl_3$ and the aqueous layer extracted with $CHCl_3$ (3×). The combined organic layers were then dried over $MgSO_4$ and evaporated to dryness. The crude product was purified as outlined in the following text.

General Procedure for the Synthesis of Dendritic Benzyl Bromides. These reactions were carried out on a scale of 0.5–10 g, as above, depending on generation number. To a solution of the appropriate dendritic benzyl alcohol (1.00 equiv) in the minimum amount of tetrahydrofuran were added CBr_4 (1.2 equiv) and triphenylphosphine (1.2 equiv), and the reaction mixture was stirred at room temperature under nitrogen. Typically, the reaction mixture would change from a transparent solution to a white solution with a precipitate forming over time. The progress of the reaction was monitored by TLC with additional amounts of carbon tetrabromide and triphenylphosphine added at 15-min intervals until reaction was complete, or until decomposition began. Decomposition was observed by the mixture turning bright yellow, followed by green and then brown if the reaction was not stopped. The reaction was quenched by addition of a large amount of water and $CHCl_3$. The aqueous layer was extracted with $CHCl_3$ (3×), and the $CHCl_3$ extracts were combined, dried, and concentrated under reduced pressure. The crude product was purified as outlined in the following text.

CN_2-[G-1]-OH (3). This was prepared from 4-(bromomethyl)-benzonitrile (**1**), and purified by flash chromatography eluting with 5% $EtOAc/CH_2Cl_2$ and recrystallization from 30% hexanes/CH_2Cl_2 to give **3** as white needle-like crystals: yield 91%; mp 144–146 °C; IR 3600–3300, 3100–2800, 2228, 1597, 1442, 1414, 1317, 1296, 1213, 1161, 1068, 1020, 816 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.70 (t, 1H, J = 6 Hz, CH_2OH), 4.64 (d, 2H, J = 6 Hz, CH_2OH), 5.10 (s, 4H, $CNPhCH_2$), 6.48 (t, 1H, J = 2 Hz, ArH), 6.61 (d, 2H, J = 2 Hz, ArH), 7.52 and 7.67 (ABq, 8H, J = 8 Hz, CNPhH); ^{13}C NMR ($CDCl_3$) δ 65.02 (CH_2OH), 68.96 (CH_2O), 101.35 (ArC), 105.83 (ArC), 111.3 (CNPhC), 118.62 (CN), 127.53, 132.42, 142.16 (CNPhC), 143.86 (ArC), 159.61 (ArC); Anal. Calcd for $C_{23}H_{18}N_2O_3$ (370.41): C, 74.58; H, 4.90; N, 7.56. Found: C, 74.35; H, 4.80; N, 7.35.

CN_2-[G-1]-Br (4). This was prepared from CN_2-[G-1]-OH (**3**), requiring 2 × 1.2 equiv of CBr_4 and PPh_3, and purified by flash chromatography eluting with 5% hexanes/CH_2Cl_2 and recrystallization from 30% hexanes/CH_2Cl_2 to give **4** as white needle-like crystals: yield 86%; mp 197–199 °C; IR 3100–2800, 2226, 1597, 1443, 1373, 1298, 1213, 1172, 1074, 1022, 835, 816 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.40 (s, 2H, CH_2Br), 5.09 (s, 4H, $CNPhCH_2$), 6.48 (t, 1H, J = 2 Hz, ArH), 6.62 (d, 2H, J = 2 Hz, ArH), 7.52 and 7.67 (ABq, 8H, J = 8 Hz, CNPhH); ^{13}C NMR ($CDCl_3$) δ 33.45 (CH_2Br), 69.03 (CH_2O), 101.80 (ArC), 106.50 (ArC), 111.84 (CNPhC), 118.60 (CN), 127.54, 132.42, 142.04 (CNPhC), 143.57 (ArC), 159.64 (ArC). Anal. Calcd for $C_{23}H_{17}BrN_2O_2$ (433.40): C, 63.74; H, 3.95; N, 6.46; Br, 18.46. Found: C, 63.82; H, 4.00; N, 6.23; Br, 18.22.

CN_4-[G-2]-OH (5). This was prepared from CN_2-[G-1]-Br (**4**) and purified by flash chromatography eluting with 5% $EtOAc/CH_2Cl_2$ to give **5** as a colorless glass: yield 93%; T_g 53 °C; IR 3600–3300, 3100–2800, 2228, 1597, 1442, 1414, 1317, 1296, 1213, 1161, 1068, 1020, 816 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.59 (t, 1H, J = 6 Hz, CH_2OH), 4.62 (d, 2H, J = 6 Hz, CH_2OH), 4.96 (s, 4H, $Ar'CH_2$), 5.09 (s, 8H, $CNPhCH_2$-), 6.42 (t, 1H, J = 2 Hz, ArH), 6.50 (t, 2H, J = 2 Hz, Ar′H), 6.61 (d, 2H, J = 2 Hz, ArH), 6.63 (d, 4H, J = 2 Hz, Ar′H), 7.50 and 7.65 (ABq, 16H, J = 8 Hz, CNPhH); ^{13}C NMR ($CDCl_3$) δ 65.10 (CH_2OH), 69.02, 69.68 (CH_2O), 101.35, 101.69 (ArC and Ar′C), 105.63, 106.47 (ArC and Ar′C), 111.82 (CNPhC), 118.60 (CN), 127.54, 132.41, 142.05 (CNPhC), 139.72, 143.55 (ArC and Ar′C), 159.61, 159.87 (ArC and Ar′C). Anal. Calcd for $C_{53}H_{40}N_4O_7$ (844.92): C, 75.34; H, 4.77; N, 6.63. Found: C, 75.51; H, 4.98; N, 6.46.

CN_4-[G-2]-Br (6). This was prepared from CN_4-[G-2]-OH (**5**), requiring 3 × 1.2 equiv of CBr_4 and PPh_3, and purified by flash chromatography eluting with 50% hexanes/CH_2Cl_2 gradually increasing to CH_2Cl_2 to give **6** as a colorless glass: yield 89%; T_g 55 °C; IR 3100–2800, 2228, 1597, 1451, 1373, 1296, 1213, 1159, 1053, 1020, 820, 756 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.39 (s, 2H, C*H*$_2$Br), 4.96 (s, 4H, Ar′C*H*$_2$), 5.10 (s, 8H, CNPhC*H*$_2$), 6.41 (t, 1H, *J* = 2 Hz, Ar*H*), 6.51 (t, 2H, *J* = 2 Hz, Ar′*H*), 6.59 (d, 2H, *J* = 2 Hz, Ar*H*), 6.63 (d, 4H, *J* = 2 Hz, Ar′*H*), 7.50 and 7.65 (ABq, 16H, *J* = 8 Hz, CNPh*H*); ^{13}C NMR ($CDCl_3$) δ 33.45 (*C*H$_2$Br), 69.03, 69.78 (*C*H$_2$O), 101.80, 102.32 (Ar*C*), 106.50, 108.11 (Ar*C*), 111.84 (CNPh*C*), 118.60 (*C*N), 127.54, 132.42, 142.04 (CNPh*C*), 139.46, 143.57 (Ar*C*), 159.64, 159.78 (Ar*C*). Anal. Calcd for $C_{53}H_{39}BrN_4O_6$ (907.91): C, 70.12; H, 4.33; N, 6.17; Br, 8.81. Found: C, 70.34; H, 4.49; N, 6.05; Br, 9.03.

CN_8-[G-3]-OH (14). This was prepared from CN_4-[G-2]-Br (**6**) and purified by flash chromatography eluting with CH_2Cl_2 to give **14** as a colorless glass: yield 94%; T_g 62 °C; IR 3600–3300, 3100–2800, 2226, 1597, 1444, 1414, 1373, 1320, 1296, 1213, 1161, 1072, 1022, 816 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.91 (t, 1H, *J* = 6 Hz, CH$_2$O*H*), 4.60 (d, 2H, *J* = 6 Hz, C*H*$_2$OH), 4.93 (s, 4H, Ar′C*H*$_2$), 4.95 (s, 8H, Ar″C*H*$_2$), 5.08 (s, 16H, CNPhC*H*$_2$), 6.43 (t, 1H, *J* = 2 Hz, Ar*H*), 6.50 (m, 6H, Ar′*H* and Ar″*H*), 6.60 (d, 2H, *J* = 2 Hz, Ar*H*), 6.61 (d, 4H, *J* = 2 Hz, Ar′*H*), 6.62 (d, 8H, *J* = 2 Hz, Ar″*H*), 7.52 and 7.67 (ABq, 8H, *J* = 8 Hz, CNPh*H*); ^{13}C NMR ($CDCl_3$) δ 64.97 (*C*H$_2$OH), 68.97, 69.43, 69.72 (*C*H$_2$O), 101.26, 101.53, 101.61 (Ar*C*), 105.59, 106.34, 106.46 (Ar*C*), 111.76 (CNPh*C*), 118.59 (*C*N), 127.48, 132.31, 141.99 (CNPh*C*), 139.38, 139.52, 143.65 (Ar*C*), 159.55, 159.78, 159.86 (Ar*C*). Anal. Calcd for $C_{113}H_{84}N_8O_{15}$ (1793.9): C, 75.66; H, 4.72; N, 6.25. Found: C, 75.45; H, 4.90; N, 5.98.

CN_8-[G-3]-Br (10). This was prepared from CN_8-[G-3]-OH (**14**), requiring 3 × 1.2 equiv of CBr_4 and PPh_3, and purified by precipitation into ether followed by flash chromatography eluting with 5% ether/CH_2Cl_2 to give **10** as a colorless glass: yield 90%; T_g 62 °C; IR 3100–2800, 2228, 1595, 1448, 1414, 1373, 1323, 1296, 1213, 1157, 1053, 1020, 820, 756 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.38 (s, 2H, C*H*$_2$Br), 4.93 (s, 4 H, Ar′C*H*$_2$), 4.96 (s, 8 H, Ar″C*H*$_2$), 5.08 (s, 16H, CNPhC*H*$_2$), 6.45 (t, 1H, *J* = 2 Hz, Ar*H*), 6.51 (m, 6H, Ar′*H* and Ar″*H*), 6.61 (d, 2H, *J* = 2 Hz, Ar*H*), 6.62 (d, 4H, *J* = 2 Hz, Ar′*H*), 6.63 (d, 8H, *J* = 2 Hz, Ar″*H*), 7.48 and 7.62 (ABq, 8H, *J* = 8 Hz, CNPh*H*); ^{13}C NMR ($CDCl_3$) δ 33.48 (*C*H$_2$Br), 68.97, 69.71, 69.96 (*C*H$_2$O), 101.59, 101.67, 102.28 (Ar*C*, Ar′*C*, and Ar″*C*), 106.43, 106.48, 108.09 (Ar*C*), 111.75 (CNPh*C*), 118.57 (*C*N), 127.50, 132.35, 142.01 (CNPh*C*), 139.04, 139.56, 139.95 (Ar*C*), 159.60, 159.87 (Ar*C*). Anal. Calcd for $C_{113}H_{83}BrN_8O_{14}$ (1856.9): C, 73.09; H, 4.51; N, 6.03; Br, 4.31. Found: C, 72.98; H, 4.74; N, 5.86; Br, 4.54.

CN_{16}-[G-4]-OH (15). This was prepared from CN_8-[G-3]-Br (**10**) and purified by flash chromatography eluting with 10% ether/CH_2Cl_2 to give **15** as a colorless glass: yield 88%; T_g 77 °C; IR 3600–3300, 3100–2800, 2228, 1597, 1448, 1414, 1343, 1323, 1298, 1213, 1159, 1055, 1020, 824, 756 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.05 (t, 1H, *J* = 6 Hz, CH$_2$O*H*), 4.55 (d, 2H, *J* = 6 Hz, C*H*$_2$OH), 4.89 (s, 4H, Ar′C*H*$_2$), 4.91 (s, 8H, Ar″C*H*$_2$), 4.93 (s, 16H, Ar‴C*H*$_2$), 5.05 (s, 32H, CNPhC*H*$_2$), 6.4–6.7 (m, 45H, Ar*H*), 7.40 and 7.53 (ABq, 64H, *J* = 8 Hz, CNPh*H*); ^{13}C NMR ($CDCl_3$) δ 64.88 (*C*H$_2$OH), 68.91, 69.65, 69.86 (*C*H$_2$O), 101.06, 101.45, 101.61 (Ar*C*), 105.57, 106.26, 106.36, 106.46 (Ar*C*), 111.64 (CNPh*C*), 118.57 (*C*N), 127.46, 132.29, 141.99 (CNPh*C*), 139.21, 139.38, 139.52, 143.78 (Ar*C*), 159.55, 159.82, 159.88, 159.94 (Ar*C*). Anal. Calcd for $C_{233}H_{172}N_{16}O_{31}$ (3692.0): C, 75.80; H, 4.70; N, 6.07. Found: C, 75.66; H, 4.81; N, 5.86.

CN_{16}-[G-4]-Br (16). This was prepared from CN_{16}-[G-4]-OH (**15**), requiring 3 × 2.0 equiv of CBr_4 and PPh_3, and purified by precipitation into ether followed by flash chromatography eluting with 10% ether/CH_2Cl_2 to give **16** as a colorless glass: yield 89%; T_g 77 °C; IR 3100–2800, 2228, 1595, 1448, 1414, 1373, 1323, 1296, 1213, 1157, 1053, 1020, 820, 756 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.34 (s, 2H, C*H*$_2$Br), 4.88 (s, 4H, Ar′C*H*$_2$), 4.92 (s, 8H, Ar″C*H*$_2$), 4.93 (s, 16H, Ar‴C*H*$_2$), 5.05 (s, 32H, CNPhC*H*$_2$), 6.4–6.7 (m, 45H, Ar*H*), 7.45 and 7.58 (ABq, 64H, *J* = 8 Hz, CNPh*H*); ^{13}C NMR ($CDCl_3$) δ 33.53 (*C*H$_2$Br), 68.93, 69.68, 69.89 (*C*H$_2$O), 101.45, 101.62, 102.10 (Ar*C*), 106.37, 106.47, 108.09, 111.10 (Ar*C*), 111.70 (CNPh*C*), 118.59 (*C*N), 127.48, 132.32, 142.00 (CNPh*C*), 139.09, 139.20, 139.53, 139.90 (Ar*C*), 159.57, 159.84, 159.97 (Ar*C*). Anal. Calcd for $C_{233}H_{171}BrN_{16}O_{30}$ (3755.0): C, 74.53; H, 4.59; N, 5.97; Br, 2.13. Found: C, 74.63; H, 4.60; N, 5.72; Br, 2.32.

General Procedure for the Synthesis of Monoalkylated Core Molecules. These preparations were carried out on a scale of 0.5–5 g depending on generation number. A mixture of the appropriate dendritic benzyl bromide[6] (1.00 equiv), 4,4′-dihydroxybiphenyl (10 equiv), potassium carbonate (10 equiv), and 18-crown-6 (1 equiv) in acetone was heated at reflux and stirred vigorously under nitrogen for 6 h. The mixture was allowed to cool and evaporated to dryness under reduced pressure. The residue was partitioned between water and $CHCl_3$ and the aqueous layer extracted with $CHCl_3$ (3×). The combined organic layers were then dried over $MgSO_4$ and evaporated to dryness. The crude product was purified as outlined in the following text.

[G-1]-[C]-OH (17). This was prepared from [G-1]-Br and purified by flash chromatography eluting with CH_2Cl_2 to give **17** as a white crystalline solid: yield 76%; mp 118–120 °C; IR 3600–3200, 3100–2800, 1595, 1499, 1453, 1375, 1296, 1240, 1159, 1030, 822, 737, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.77 (s, 1H, coreO*H*), 5.03 (s, 2H, ArC*H*$_2$), 5.04 (s, 4H, PhC*H*$_2$), 6.57 (t, 1H, *J* = 2 Hz, Ar*H*), 6.70 (d, 2H, *J* = 2 Hz, Ar*H*), 6.87 (A of ABq, 2H, *J* = 8 Hz, core*H*), 6.99 (A of ABq, 2H, *J* = 8 Hz, core*H*), 7.3–7.6 (m, 14H, Ph*H*(10) and core*H*(4)); ^{13}C NMR ($CDCl_3$) δ 69.98, 70.09 (*C*H$_2$O), 101.55 (Ar*C*), 106.35 (Ar*C*), 115.12, 115.56, 127.53, 127.88 (core*C*), 127.49, 127.97, 128.55 (Ph*C*), 133.49, 133.66 (core*C*), 136.72 (Ph*C*), 139.19 (Ph*C*), 154.62, 157.75 (core*C*), 160.12 (Ar*C*). Anal. Calcd for $C_{33}H_{28}O_4$ (488.6): C, 81.13; H, 5.78. Found: C, 81.19; H, 5.97.

[G-2]-[C]-OH (18). This was prepared from [G-2]-Br and purified by flash chromatography eluting with CH_2Cl_2 to give **18** as a white solid: yield 82%; mp 116 °C; IR 3600–3200, 3100–2800, 1595, 1498, 1453, 1375, 1296, 1240, 1159, 1035, 822, 737, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.92 (s, 2H, ArC*H*$_2$), 4.98 (s, 4H, Ar′C*H*$_2$), 5.03 (s, 8H, PhC*H*$_2$), 6.57 (m, 3H, Ar*H*), 6.69 (d, 6H, *J* = 2 Hz, Ar*H* and Ar′*H*), 6.85 (A of ABq, 2H, *J* = 8 Hz, core*H*), 6.99 (A of ABq, 2H, *J* = 8 Hz, core*H*), 7.3–7.5 (m, 24 H, Ph*H*(20) and core*H*(4)); ^{13}C NMR ($CDCl_3$) δ 69.97, 70.08 (*C*H$_2$O), 101.54, 101.58, 106.34, 106.37 (Ar*C*), 115.12, 115.56, 127.53, 127.88 (core*C*), 127.49, 127.97, 128.55 (Ph*C*), 133.49, 133.66 (core*C*), 136.72 (Ph*C*), 139.19, 139.51 (Ar*C*), 154.62, 157.75 (core*C*), 160.02, 160.12 (Ar*C*). Anal. Calcd\ for $C_{61}H_{52}O_8$ (913.1): C, 80.24; H, 5.74. Found: C, 80.37; H, 5.47.

[G-3]-[C]-OH (19). This was prepared from [G-3]-Br and purified by flash chromatography eluting with CH_2Cl_2 to give **19** as a colorless glass: yield 77%; T_g 41 °C; IR 3600–3200, 3100–2800, 1595, 1498, 1451, 1373, 1296, 1155, 1051, 830, 737, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.95, 4.96, 4.99, 5.00 (each s, 30H, ArC*H*$_2$), 6.5–6.6 (m, 7H, Ar*H*), 6.65–6.7 (m, 14H, Ar*H*), 6.82 (A of ABq, 2H, *J* = 8 Hz, core*H*), 6.96 (A of ABq, 2H, *J* = 8 Hz, core*H*), 7.25–7.45 (m, 44H, Ph*H*(40) and core*H*(4)); ^{13}C NMR ($CDCl_3$) δ 69.96, 70.07 (*C*H$_2$O), 101.53, 101.58, 106.36, 106.40 (Ar*C*), 115.14, 115.56, 127.65, 127.93 (core*C*), 127.53, 127.98, 128.53 (Ph*C*), 133.53, 133.64 (core*C*), 136.74 (Ph*C*), 139.19, 139.21, 139.54 (Ar*C*), 154.60, 157.75 (core*C*), 160.03, 160.05, 160.13 (Ar*C*). Anal. Calcd for $C_{117}H_{100}O_{16}$ (1762): C, 79.75; H, 5.72. Found: C, 79.61; H, 5.91.

[G-4]-[C]-OH (9). This was prepared from [G-4]-Br and purified by flash chromatography eluting with CH_2Cl_2 to give **9** as a colorless glass: yield 64%; T_g 46 °C; IR 3600–3200, 3100–2800, 1595, 1498, 1451, 1375, 1296, 1155, 1051, 830, 737, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.92, 4.98, 5.02 (each s, 62H, ArC*H*$_2$), 6.5–6.6 (m, 15H, Ar*H*), 6.6–6.7 (m, 30H, Ar*H*), 6.77 (A of ABq, 2H, *J* = 8 Hz, core*H*), 6.92 (A of ABq, 2H, *J* = 8 Hz, core*H*), 7.25–7.45 (m, 84H, Ph*H*(80) and core*H*(4)); ^{13}C NMR ($CDCl_3$) δ 69.90, 70.00 (*C*H$_2$O), 101.55, 106.34 (Ar*C*), 115.09, 115.54, 127.77, 127.92 (core*C*), 127.49, 128.29, 128.50 (Ph*C*), 133.50, 133.61 (core*C*), 136.71 (Ph*C*), 139.17, 139.26, 139.51 (Ar*C*), 154.62, 157.65 (core*C*), 159.98, 160.07 (Ar*C*). Anal. Calcd for $C_{229}H_{196}O_{32}$ (3460): C, 79.49; H, 5.71. Found: C, 79.28; H, 5.80.

[G-5]-[C]-OH (20). This was prepared from [G-5]-Br and purified by chromatotron (5×) eluting with CH_2Cl_2 gradually increasing to <1% ether/CH_2Cl_2 to give **20** as a colorless glass: yield 43% ([G-5]-[C]-[G-5] also obtained in 12% yield); T_g 48 °C; IR 3600–3200, 3100–2800, 1595, 1498, 1451, 1373, 1296, 1155, 1051, 830, 737, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.90, 4.94, 4.97, 5.03 (each s, 126H, ArC*H*$_2$), 6.4–6.8 (m, 93H, Ar*H*), 6.8 (A of ABq, 2H, *J* = 8 Hz, core*H*), 6.9 (A of ABq, 2H, *J* = 8 Hz, core*H*), 7.1–7.5 (m, 164H, Ph*H*(160) and core*H*(4)); ^{13}C NMR ($CDCl_3$) δ 69.93 (*C*H$_2$O), 101.50, 106.30 (Ar*C*), 115.07, 115.52, (core*C*), 127.77, 127.85 (peaks too small to observe, core*C*), 127.47, 127.87, 128.46 (Ph*C*), 133.50, 133.61 (peaks too small to observe, core*C*), 136.70 (Ph*C*), 139.15 (Ar*C*), 154.62, 157.65 (peaks too small to observe, core*C*), 159.94, 160.03 (Ar*C*). Anal. Calcd for $C_{453}H_{388}O_{64}$ (6856): C, 79.36; H, 5.70. Found: C, 79.20; H, 5.30.

General Procedure for the Synthesis of Dialkylated Core Molecules. These preparations were carried out on a scale of 0.2–2 g depending on generation number. A mixture of the appropriate dendritic benzyl bromide

(2.2 equiv), 4,4′-dihydroxybiphenyl (1.0 equiv), K_2CO_3 (2.5 equiv), and 18-crown-6 (0.3 equiv) in acetone was heated at reflux and stirred vigorously under nitrogen for 12 h. The mixture was allowed to cool and evaporated to dryness under reduced pressure. The residue was partitioned between water and $CHCl_3$ and the aqueous layer extracted with $CHCl_3$ (3×). The combined organic layers were then dried over $MgSO_4$ and evaporated to dryness. The crude product was purified as outlined in the following text.

[G-0]-[C]-[G-0] (21). This was prepared from benzyl bromide and purified by flash chromatography eluting with 25% hexanes/CH_2Cl_2 gradually increasing to CH_2Cl_2 to give **21** as a white crystalline solid. This product was too insoluble in benzene to allow measurement of the dipole moment: yield 88%; mp 203–205 °C; IR 3100–2800, 1595, 1498, 1453, 1375, 1294, 1238, 1158, 1036, 823, 737, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.09 (s, 4H, PhCH_2O), 7.02 (A of ABq, 4H, J = 8 Hz, core*H*), 7.3–7.5 (m, 14H, Ph*H*(10) and core*H*(4)); ^{13}C NMR ($CDCl_3$) δ 69.90 (*C*H$_2$O), 115.18, 127.75 (core*C*), 127.49, 128.29, 128.50 (Ph*C*), 133.70 (core*C*), 136.71 (Ph*C*), 157.82 (core*C*). Anal. Calcd for $C_{26}H_{22}O_2$ (366.5): C, 85.22; H, 6.05. Found: C, 85.07; H, 5.85.

[G-1]-[C]-[G-1] (22). This was prepared from [G-1]-Br and purified by flash chromatography eluting with 10% hexanes/CH_2Cl_2 gradually increasing to CH_2Cl_2 to give **22** as a white crystalline solid: yield 93%; mp 92–94 °C; IR 3100-2800, 1596, 1498, 1454, 1377, 1293, 1238, 1159, 1038, 823, 7367, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.97, 5.02 (each s, 12H, ArCH_2), 6.55 (t, 2H, J = 2 Hz, Ar*H*), 6.66 (d, 4H, J = 2 Hz, Ar*H*), 6.98 (A of ABq, 4H, J = 8 Hz, core*H*), 7.3–7.5 (m, 24H, Ph*H*(20) and core*H*(4)); ^{13}C NMR ($CDCl_3$) δ 69.98, 70.09 (*C*H$_2$O), 101.59, 106.39 (Ar*C*), 115.14, 127.71 (core*C*), 127.53, 128.01, 128.54 (Ph*C*), 133.68 (core*C*), 136.71 (Ph*C*), 139.22, 139.51 (Ar*C*), 157.81 (core*C*), 160.07 (Ar*C*). Anal. Calcd for $C_{54}H_{46}O_6$ (790.9): C, 82.00; H, 5.86. Found: C, 82.38; H, 6.02.

[G-2]-[C]-[G-2] (23). This was prepared from [G-2]-Br and purified by flash chromatography eluting with 25% hexanes/CH_2Cl_2 gradually increasing to CH_2Cl_2 to give **23** as a colorless glass: yield 92%; T_g 33 °C; IR 3100–2800, 1596, 1498, 1453, 1375, 1295, 1238, 1157, 1054, 827, 737, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.98, 5.02 (each s, 28H, ArCH_2), 6.56 (m, 6H, Ar*H*), 6.68 (m, 12H, Ar*H*), 6.98 (A of ABq, 4H, J = 8 Hz, core*H*), 7.3–7.5 (m, 44H, Ph*H*(40) and core*H*(4)); ^{13}C NMR ($CDCl_3$) δ 69.99, 70.10 (*C*H$_2$O), 101.59, 106.37 (Ar*C*), 115.13, 127.71 (core*C*), 127.54, 127.99, 128.57 (Ph*C*), 133.68 (core*C*), 136.75 (Ph*C*), 139.22, 139.53 (Ar*C*), 157.81 (core*C*), 160.06, 160.16 (Ar*C*). Anal. Calcd for $C_{110}H_{94}O_{14}$ (1640): C, 80.57; H, 5.78. Found: C, 80.87; H, 5.91.

[G-3]-[C]-[G-3] (24). This was prepared from [G-3]-Br and purified by flash chromatography eluting with 25% hexanes/CH_2Cl_2 gradually increasing to CH_2Cl_2 to give **24** as a colorless glass: yield 84%; T_g 38 °C; IR 3100–2800, 1596, 1498, 1451, 1375, 1295, 1217, 1155, 1053, 831, 737, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.97, 5.02 (each s, 60H, ArCH_2), 6.57 (m, 14H, Ar*H*), 6.69 (m, 28H, Ar*H*), 6.98 (A of ABq, 4H, J = 8 Hz, core*H*), 7.3–7.5 (m, 84H, Ph*H*(80) and core*H*(4)); ^{13}C NMR ($CDCl_3$) δ 69.99 (*C*H$_2$O), 101.54, 106.32 (Ar*C*), 115.01, 127.72 (core*C*), 127.48, 127.91, 128.49 (Ph*C*), 133.73 (core*C*), 136.71 (Ph*C*), 139.17 (Ar*C*), 157.81 (core*C*), 159.99, 160.08 (Ar*C*). Anal. Calcd for $C_{222}H_{190}O_{30}$ (3338): C, 79.88; H, 5.74. Found: C, 80.04; H, 5.79.

[G-4]-[C]-[G-4] (12). This was prepared from [G-4]-Br and purified by flash chromatography eluting with CH_2Cl_2 to give **12** as a colorless glass: yield 84%; T_g 38 °C; IR 3100–2800, 1596, 1498, 1451, 1375, 1295, 1217, 1155, 1053, 831, 737, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.92, 4.98 (each s, 124H, ArCH_2), 6.55 (m, 30H, Ar*H*), 6.66 (m, 60H, Ar*H*), 6.93 (A of ABq, 4H, J = 8 Hz, core*H*), 7.25-7.45 (m, 164 H, Ph*H*(160) and core*H*(4)); ^{13}C NMR ($CDCl_3$) δ 69.99 (*C*H$_2$O), 101.54, 106.32 (Ar*C*), 115.01, 127.7 (core*C*), 127.48, 127.91, 128.49 (Ph*C*), 133.7 (core*C*), 136.71 (Ph*C*), 139.17 (Ar*C*), 157.8 (core*C*), 159.99, 160.08 (Ar*C*). Anal. Calcd for $C_{446}H_{382}O_{62}$ (6734): C, 79.55; H, 5.72. Found: C, 79.63; H, 5.89.

[G-5]-[C]-[G-5] (25). This was prepared from [G-5]-Br, and purified by flash chromatography eluting with CH_2Cl_2 to give **25** as a colorless glass: yield 80%; T_g 39 °C; IR 3100–2800, 1596, 1498, 1451, 1375, 1295, 1217, 1155, 1053, 831, 737, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.92, 4.98 (each s, 124H, ArCH_2), 6.55 (m, 30H, Ar*H*), 6.66 (m, 60H, Ar*H*), 6.93 (A of ABq, 4H, J = 8 Hz, core*H*), 7.25–7.45 (m, 164H, Ph*H*(160) and core*H*(4)); ^{13}C NMR ($CDCl_3$) δ 69.99 (*C*H$_2$O), 101.54, 106.32 (Ar*C*), 115.01, 127.7 (core*C*), 127.48, 127.91, 128.49 (Ph*C*), 133.7 (core*C*), 136.71 (Ph*C*), 139.17 (Ar*C*), 157.8 (core*C*), 159.99, 160.08 (Ar*C*). Anal. Calcd for $C_{894}H_{766}O_{126}$ (13 526): C, 79.39; H, 5.71. Found: C, 79.56; H, 5.80.

General Procedure for the Synthesis of Dipolar Dendritic Molecules. These preparations were carried out on a scale of 0.2–2 g depending on generation number. A mixture of the appropriate cyano-terminated dendritic benzyl bromide (1.0 equiv), the appropriate monoalkylated core (1.2 equiv), K_2CO_3 (2.5 equiv), and 18-crown-6 (0.3 equiv) in THF was heated at reflux and stirred vigorously under nitrogen for 12 h. The mixture was allowed to cool and evaporated to dryness under reduced pressure. The residue was partitioned between water and $CHCl_3$ and the aqueous layer extracted with $CHCl_3$ (3×). The combined organic layers were then dried over $MgSO_4$ and evaporated to dryness. The crude product was purified as outlined in the following text.

CN-[G-0]-[C]-[G-1] (26). This was prepared from 4-(bromomethyl)-benzonitrile **1** and [G-1]-[C]-OH (**17**) and purified by flash chromatography eluting with 25% hexanes/CH_2Cl_2 to give **26** as a white crystalline solid: yield 89%; mp 166–168 °C; IR 3100–2800, 2226, 1597, 1499, 1447, 1379, 1242, 1167, 1053, 826 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.03 (s, 2H, ArCH_2), 5.04 (s, 4H, PhCH_2), 5.15 (s, 2H, CNPhCH_2), 6.58 (t, 1H, J = 2 Hz, Ar*H*), 6.70 (d, 2H, J = 2 Hz, Ar*H*), 6.99 (A of ABq, 2H, J = 8 Hz, core*H*), 7.01 (A of ABq, 2H, J = 8 Hz, core*H*), 7.3–7.5 (m, 14H, Ph*H*(10) and core*H*(4)), 7.56 (A of ABq, 2H, J = 8 Hz, CNPh*H*), 7.68 (B of ABq, 2H, J = 8 Hz, CNPh*H*); ^{13}C NMR ($CDCl_3$) δ 68.98, 69.97, 70.11 (*C*H$_2$O), 101.49, 106.30 (Ar*C*), 111.3 (CNPh*C*), 115.05, 115.16, 127.76, 127.86 (core*C*), 118.62 (*C*N), 127.53, 128.02, 128.58 (Ph*C*), 127.55, 132.42, 142.16 (CNPh*C*), 133.41, 133.43 (core*C*), 136.73 (Ph*C*), 139.17 (Ar*C*), 157.27, 157.93 (core*C*), 160.16 (Ar*C*). Anal. Calcd for $C_{41}H_{33}NO_4$ (603.7): C, 81.57; H, 5.51; N, 2.32. Found: C, 81.80; H, 5.56; N, 2.17.

CN_2-[G-1]-[C]-[G-2] (27). This was prepared from CN_2-[G-1]-Br (**4**) and [G-2]-[C]-OH (**18**) and purified by flash chromatography eluting with 10% hexanes/CH_2Cl_2 gradually increasing to CH_2Cl_2 to give **27** as a colorless glass: yield 77%; T_g 40 °C; IR 3100–2800, 2228, 1597, 1499, 1453, 1377, 1294, 1238, 1157, 1051, 824, 741, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.97 (s, 4H, ArCH_2), 5.02 (s, 12H, PhCH_2), 5.10 (s, 4H, CNPhCH_2), 6.51–6.56 (m, 4H, Ar*H*), 6.67–6.70 (m, 8H, Ar*H*), 6.97 (A of ABq, 2H, J = 8 Hz, core*H*), 7.00 (A of ABq, 2H, J = 8 Hz, core*H*), 7.3–7.5 (m, 24H, Ph*H*(20) and core*H*(4)), 7.52 (A of ABq, 2H, J = 8 Hz, CNPh*H*), 7.66 (B of ABq, 2H, J = 8 Hz, CNPh*H*); ^{13}C NMR ($CDCl_3$) δ 69.01, 69.75, 69.98, 70.10 (*C*H$_2$O), 101.52, 101.58, 101.67, 106.37, 106.46 (Ar*C*), 111.83 (CNPh*C*), 115.05, 115.19, 127.69, 127.74 (core*C*), 118.60 (*C*N), 127.53, 127.98, 128.56 (Ph*C*), 127.56, 132.41, 142.07 (CNPh*C*), 133.41, 133.48 (core*C*), 136.75 (Ph*C*), 139.20, 139.49, 140.06 (Ar*C*), 157.61, 157.90 (core*C*), 159.64, 160.06, 160.16 (Ar*C*). Anal. Calcd for $C_{84}H_{68}N_2O_{10}$ (1266): C, 79.72; H, 5.42; N, 2.21. Found: C, 79.93; H, 5.13; N, 1.94.

CN_4-[G-2]-[C]-[G-3] (28). This was prepared from CN_4-[G-2]-Br (**6**) and [G-3]-[C]-OH (**19**) and purified by flash chromatography eluting with 1% ether/CH_2Cl_2 to give **28** as a colorless glass: yield 78%; T_g 53 °C; IR 3100–2800, 2228, 1597, 1497, 1453, 1379, 1294, 1238, 1157, 1051, 824, 746, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.94, 4.96, 4.97 (each s, 20H, ArCH_2), 4.99 (s, 16H, PhCH_2), 5.08 (s, 8H, CNPhCH_2), 6.50–6.55 (m, 10H, Ar*H*), 6.63–6.68 (m, 20H, Ar*H*), 6.93 (A of ABq, 2H, J = 8 Hz, core*H*), 6.94 (A of ABq, 2H, J = 8 Hz, core*H*), 7.25–7.45 (m, 44H, Ph*H*(40) and core*H*(4)), 7.48 (A of ABq, 2H, J = 8 Hz, CNPh*H*), 7.63 (B of ABq, 2H, J = 8 Hz, CNPh*H*); ^{13}C NMR ($CDCl_3$) δ 68.99, 69.73, 69.97, 70.07 (*C*H$_2$O), 101.58, 101.71, 106.36, 106.42, 106.47 (Ar*C*), 111.80 (CNPh*C*), 115.05, 115.17, 127.71, 127.74 (core*C*), 118.60 (*C*N), 127.53, 127.98, 128.55 (Ph*C*), 127.64, 132.39, 142.02 (CNPh*C*), 133.42, 133.81 (core*C*), 136.74 (Ph*C*), 139.19, 139.48, 139.66 (Ar*C*), 157.69, 157.88 (core*C*), 159.62, 159.88, 160.04, 160.13 (Ar*C*). Anal. Calcd for $C_{170}H_{138}N_4O_{22}$ (2589): C, 78.87; H, 5.37; N, 2.16. Found: C, 79.02; H, 5.61; N, 1.89.

CN_8-[G-3]-[C]-[G-4] (11). This was prepared from CN_8-[G-3]-Br (**10**) and [G-4]-[C]-OH (**9**) and purified by flash chromatography eluting with 2% ether/CH_2Cl_2 to give **11** as a colorless glass: yield 73%; T_g 55 °C; IR 3100–2800, 2228, 1597, 1499, 1451, 1375, 1296, 1238, 1159, 1053, 828, 752, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.89, 4.93 (each s, 44H, ArCH_2), 4.94 (s, 32H, PhCH_2), 5.04 (s, 16H, CNPhCH_2), 6.4–6.5 (m, 22H, Ar*H*), 6.6–6.65 (m, 44H, Ar*H*), 6.90 (A of ABq, 4H, J = 8 Hz, core*H*), 7.2–7.4 (m, 84H, Ph*H*(80) and core*H*(4)), 7.44 (A of ABq, 2H, J = 8 Hz, CNPh*H*), 7.59 (B of ABq, 2H, J = 8 Hz, CNPh*H*); ^{13}C NMR ($CDCl_3$) δ 68.96, 69.71, 69.92, 70.02 (*C*H$_2$O), 101.55, 101.67, 106.34, 106.47 (Ar*C*), 111.76 (CNPh*C*), 115.03, 115.13, 127.69, 127.71 (core*C*), 118.59 (*C*N), 127.51, 127.95, 128.53 (Ph*C*), 127.62, 132.36, 141.99 (CNPh*C*), 133.42, 133.81 (core*C* peaks too small to observe), 136.73 (Ph*C*), 139.18, 139.27, 139.58 (Ar*C*), 157.69, 157.88 (core*C* peaks too small to observe), 159.60, 159.87, 160.01, 160.09 (Ar*C*). Anal. Calcd for $C_{342}H_{278}N_8O_{46}$ (5236): C, 78.45; H, 5.35; N, 2.14. Found: C, 78.81; H, 5.62; N, 1.97.

CN_{16}-[G-4]-[C]-[G-5] (13). This was prepared from CN_{16}-[G-4]-Br (**16**) and [G-5]-[C]-OH (**20**) and purified by chromatotron eluting with 5% ether/CH_2Cl_2 gradually increasing to <10% ether/CH_2Cl_2 to give **13** as a colorless glass: yield 71%; T_g 56 °C; IR 3100–2800, 2228, 1597, 1499, 1453, 1376, 1296, 1238, 1159, 1051, 828, 752, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.84, 4.91 (each s, 156H, ArC*H*$_2$ and PhC*H*$_2$) 5.01 (s, 32H, CNPhC*H*$_2$), 6.4–6.55 (m, 46H, Ar*H*), 6.55–6.65 (m, 92H, Ar*H*), 6.86 (A of ABq, 4H, J = 8 Hz, core*H*), 7.15–7.35 (m, 164H, Ph*H*(160) and core*H*(4)), 7.42 (A of ABq, 2H, J = 8 Hz, CNPh*H*), 7.56 (B of ABq, 2H, J = 8 Hz, CNPh*H*); ^{13}C NMR ($CDCl_3$) δ 68.85, 69.91 (*C*H$_2$O), 101.45, 101.56, 106.28, 106.43 (Ar*C*), 111.63 (CNPh*C*), 115.03, 115.13, 127.69, 127.71 (core*C* peaks too small to observe), 118.58 (*C*N), 127.47, 127.89, 128.48 (Ph*C*), 127.47, 132.28, 141.93 (CNPh*C*), 133.42, 133.81 (core*C* peaks too small to observe), 136.68 (Ph*C*), 139.14, 139.20, 139.51 (Ar*C*), 157.69, 157.88 (core*C* peaks too small to observe), 159.54, 159.82, 159.93, 160,02 (Ar*C*). Anal. Calcd for $C_{686}H_{558}N_{16}O_{94}$ (10 530): C, 78.25; H, 5.34; N, 2.13. Found: C, 78.39; H, 5.39; N, 2.01.

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